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**(54) Verfahren zur antistatischen Ausrüstung von Schmelzkleber-Schichten**

Erfindungsgemäß werden mit einer antistatischen Schmelzkleber-Schicht versehene Kunststoff-Formteile dadurch erhalten, daß man die Schmelzkleber-Schicht durch Beschichten mit einer gegebenenfalls Bindemittel enthaltenden Lösung einer löslichen elektrisch leitfähigen Verbindung oder einer gegebenenfalls Bindemittel enthaltenden Dispersion eines elektrisch leitfähigen, fein verteilten Feststoffes und nachfolgendes Entfernen des Lösungs- bzw. Dispergiermittels mit einer 0,05 bis 5 µm dicken, 10 bis 100 Gew.-% bezogen auf das Trockengewicht der Antistatikbeschichtung, elektrisch leitfähige Verbindungen bzw. Feststoffe enthaltenden Schicht versieht.

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Process for Antistatically Finishing Hot-Melt Adhesive Layers

Abstract

According to the invention, molded plastic articles equipped with an antistatic hot-melt adhesive layer are obtained by providing the hot-melt adhesive layer with a 0.05-5 $\mu$ m-thick layer, which makes up 10-100% by weight, relative to the dry weight of the antistatic layer and contains electrically conductive compounds or solid materials--by coating with a solution of an soluble electrically conductive compound that possibly contains a bonding agent, or a dispersion of an electrically conductive, finely dispersed solid material that possibly contains a bonding agent, and subsequently removing the solvent or the dispersing medium.

Description

The invention relates to a process for antistatically finishing hot-melt adhesive layers on molded plastic articles.

Packaging materials with an antistatic finish are increasingly used for packing electronic components, to prevent damage to the components by static charge. The surface resistance of these packaging materials should lie between  $R_{sb} = 10^4 \Omega$  and  $10^9 \Omega$ . Presently, belt bands (see Fig. 1) are used especially for electronic components. These belt bands consist of antistatically finished plastic bands (1) into which small troughs that accommodate the electronic components (2) are pressed by cold-forming or deep-drawing.

To secure the components against dropping out, the troughs are closed off by sealing them with a heat-sealable plastic foil (3). The antistatically finished plastic bands (1) used as belt bands can consist, e.g., of soot-filled plastics. As cover foils (3) plastic foils are used that are equipped with an hot-melt adhesive layer (5) [see Fig. 2].

Until now these plastic films equipped with a hot-melt adhesive layer have not been finished antistatically because of the fear that, because of an antistatic finish, the hot-melt adhesive layers would lose their adhesiveness or that the adhesiveness at least would be too strongly impaired. In addition, the experience with the moderate thermal resistance of the antistatics used until now for the antistatic finish of plastics justify the expectation that, because of the temperatures usually applied during the heat sealing (melting), the antistatic finish will at least be strongly reduced, if not lost.

However, because an effective protection of the packaged parts against electrostatic charge is only guaranteed if not only the belt bands (1) but also the sealing films (3) are finished antistatically, the task was to find a process with which it is possible to produce plastic films equipped with an antistatic hot-melt adhesive layer that meet the requirements made of that type of sealing film--namely, that, even after heat sealing, still exhibit a surface resistance of  $10^1$  to  $10^9 \Omega$  and, moreover, an adhesiveness that is evenly distributed over the entire surface of the hot-melt adhesive layer. Also the last-mentioned requirement--the evenly distributed adhesiveness--is an important feature because the sealing films must allow automatic removal--that is, with a tensile force adjusted to a specific value.

Surprisingly, it was discovered that molded plastic articles such as plastic foils equipped with an antistatic hot-melt adhesive layer with a uniform adhesiveness are obtained in a simple way that also can be implemented on an industrial scale if the molded plastic articles equipped with the hot-melt adhesive layer are provided with a  $0.05\text{--}5 \mu\text{m}$ -thick layer--which makes up 10-100% by weight, relative to the dry weight of the antistatic layer and contains electrically conductive compounds or solid materials--by coating it with a solution of a soluble, electrically conductive compound that, possibly, contains a bonding agent or a dispersion of an electrically conductive-finely dispersed solid material that possibly contains a bonding agent, and subsequently removing the solvent or the dispersing medium.

If this layer thickness and the minimum contents of electrically conductive compounds are preserved, molded plastic articles--preferably, plastic foils--equipped with hot-melt adhesive layers are obtained that fully meet the requirements made of sealing films for heat sealing--namely, that they have high adhesiveness evenly distributed over the entire hot-melt adhesive layer and, simultaneously, surface resistance values in the range of  $10^2$  -  $10^9 \Omega$ .

Also transparent antistatic coatings of the hot-melt adhesive layers can be obtained according to the process of the invention as a function of the transparency of the antistatic used for the coating. Therefore, if transparent hot-melt adhesives and transparent carrier films are used, the process according to the invention allows a production of transparent sealing films, provided with antistatic hot-melt adhesive layers, that permit optical control of the sealed plastic packagings.

Therefore, the invention relates to a process for the production of molded plastic articles equipped with an antistatic hot-melt adhesive layer that is characterized in that the hot-melt adhesive layer is provided with a layer comprising electrically conductive compounds or solid materials, with a thickness of

0.05 - 5  $\mu\text{m}$ --preferably, 0.05 - 2  $\mu\text{m}$ --and making up 10-100% by weight--preferably 30-80% by weight--relative to the dry weight of the antistatic coating, by coating the hot-melt adhesive layer with a solution of a soluble electrically conductive compound that possibly contains a bonding agent, or a dispersion of an electrically conductive, finely dispersed solid material that possibly contains a bonding agent, and subsequently removing the solvent or the dispersing medium.

Soluble electrically conductive compounds suitable for antistatically finishing the hot-melt adhesive layers are, e.g., polyanilinium salts as they are described in DE-AS 22 62 743, or soluble electrically conductive polyheteroaromatics (polypyrroles or polythiophenes) as they are described, e.g., in EP-A 2 57 573.

Electrically conductive, finely distributed solid materials suitable for the antistatic finishing of hot-melt adhesive layers are, e.g., high conductivity soots, electrically conductive metal oxides such as antimony-doped tin dioxide and zinc oxide, and metal powders such as copper- and silver powder. Preferably, the electrically conductive, finely distributed solid materials have a particle size smaller than 1  $\mu\text{m}$ --preferably smaller than 0.1  $\mu\text{m}$ . The production of dispersions of electrically conductive, finely distributed solid materials that are suitable for the process according to the invention has been described, e.g., in DE-OS 37 08 706 and in ANTEC 187, pp. 386-390.

The dry film thickness--that is, the thickness after drying of the antistatic coating to be applied according to the invention--is 0.05 - 5.0  $\mu\text{m}$ , corresponding to a wet-film thickness of about 0.1  $\mu\text{m}$  - 100  $\mu\text{m}$ . Within the specified range, the dry film thickness has to be attuned to the thickness of the hot-melt adhesive layer in such a manner that the dry film thickness of the antistatic coating is maximally 50%--preferably, 2-50%--of the thickness of the hot-melt adhesive layer. Greater thicknesses can have a detrimental effect on the adhesiveness of the hot-melt adhesive layers and, in some cases, even on the electrical conductivity of the antistatic coatings.

The solutions or dispersions used in the process according to the invention preferably contain bonding agents to increase the adhesion to the hot-melt adhesive layer. Suitable bonding agents are, e.g., synthetic organic polymers, soluble in organic solvents such as polyvinyl acetate, polycarbonate, polyvinyl alcohol, polyvinyl butyral, polyacrylic acid ester, polymethacrylic acid ester, polystyrene, polyacrylonitrile, polyvinyl chloride, polybutadiene, polyisoprene, polyether, polyester, and silicones; also copolymers soluble in organic solvents such as styrene/acrylic acid ester-, vinyl acetate/acrylic acid ester-, and ethylene/vinyl acetate copolymerizates can be used.

Preferred bonding agents are: polyvinyl acetate, polycarbonate, poly(meth)acrylic acid ester, and copolymerizates of the monomers on which these polymers are based.

The selection of the solvents or dispersing media used for the production of the solutions or dispersions is determined by the anticipated electrically conductive compounds or the electrically conductive finely distributed solid material, the optionally provided bonding agent, and the hot-melt adhesive to be coated.

Suitable solvents (dispersing media) must readily dissolve the bonding agent if such agent is used, and also readily dissolve soluble antistatics if they are used, but they may not lead to any damage to the hot-melt adhesive to be coated.

As examples of solvents with the required properties should be mentioned: water; aliphatic alcohols such as methanol, ethanol, or isopropanol; aliphatic ketones such as acetone, methylethyl ketone, and cyclohexanone; aliphatic carboxylic acid esters such as acetic acid methyl-, and acetic acid butyl esters; aromatic hydrocarbons such as toluene and xylene; halogenated hydrocarbons such as dichloromethane and dichloroethane; and aliphatic nitriles such as acetonitrile.

Depending on the used electrically conductive compound or the electrically conductive, finely distributed solid material, the bonding agent content of the coating solutions or -dispersions is generally 0-9 parts by weight--preferably 0.25-2.3 parts by weight--a bonding agent per part by weight of the conductive compound or conductive solid material.

Suitable methods for coating the hot-melt adhesive layer to be finished antistatically and possibly the surface of the plastic molded article that is not covered by the hot-melt adhesive are: spraying, knife-coating, brushing, and imprinting (e.g., in rotogravure).

After coating the hot-melt adhesive layers with the solutions or dispersions of the electrically conductive compounds or materials, the solvents or dispersing media are removed by evaporation (drying)--possibly at increased temperatures.

With the aid of the process according to the invention, the plastic molded article on which the hot-melt adhesive layer is located, can also be antistatically finished simultaneously with the hot-melt adhesive layer. In this case, not only the hot-melt adhesive layer is treated as described in the preceding, but also the entire molded article that has been provided with the hot-melt adhesive layer.

If, in the case of the molded article, it concerns a foil, the antistatically finished foil described in Fig. 3 that is provided with an antistatic hot-melt adhesive layer is obtained.

Above all, the following plastics are suitable as carrier materials for the hot-melt adhesive layers to be finished according to the invention: polycarbonates; polyamides; polyurethanes; polyureas; polyesters; polyethers; polyolefins such as polypropylene; polyethylene; polyvinyl chloride; polymethacrylic acid esters; polystyrene; or cellulose ester and -ether.

By "hot-melt adhesives" are understood, within the framework of the invention, adhesives that cure without chemical reaction; to these adhesives that cure without a chemical reaction belong, on the one hand, the real hot-melt adhesives and, on the other hand, heat-sealing adhesives and high-frequency (HF)-auxiliary welding materials. The real hot-melt adhesives are solvent-free adhesives that, when hot and in a liquid state, can readily wet the surfaces of the materials and adhere tightly to them after chilling and solidifying. During the melting process, they do not suffer any chemical change.

As example for real hot-melt adhesives should be mentioned: fusible, high-molecular ethylene-vinyl acetate copolymers and mixtures of about equal parts of ethylene-vinyl acetate copolymers with resins (gum rosin, colophony derivatives, and hydrocarbon resins) and waxes or paraffins. The hot-melt adhesives are processed at temperatures between 100 and 190°C.

The heat-sealing adhesives and high-frequency auxiliary welding materials are coating adhesives that are mainly applied to the plastics in the form of adhesive solutions. Prior to the adhesive procedure, the solvent is removed. The hardened solvent-free layer is melted by supply of heat during the sealing or, in the case of high-frequency auxiliary welding materials, molten in an electric field by heat build-up in the adhesive layer.

As heat-sealing adhesives should be mentioned, by way of example: copolymers of vinyl chloride or of vinyl idene chloride; furthermore, copolymers of vinyl acetate as well as polymethacrylic acid esters, polyurethanes, and polyesters (see Ullmanns Enzyklopädie der technischen Chemie, 4th ed., vol. 14, pp. 236-238).

#### Example 1

A solution of 0.2 g of emeraldine hydrochloride and 0.1 g of polyvinyl acetate in 15 ml of methanol are applied by knife coating with a hand coater--(Wet-film thickness: about 24  $\mu\text{m}$ , corresponding to a dry-film thickness of 1-2  $\mu\text{m}$ )--onto a polyamide film coated on one side with hot-melt adhesive (Buklin laminated film consisting of OA/e 1514 of the Bischoff & Klein Company).

After evaporation of the solvent, a hot-melt adhesive layer equipped with a transparent antistatic layer is obtained that can easily be bonded. The surface resistance of the hot-melt adhesive layer is  $10^6 \Omega$ .

The film can be tightly sealed onto another plastic film, e.g., a polyamide film, by heat sealing at  $120^\circ\text{C}$ .

The polyanilinium salt emeraldine hydrochloride used as a soluble electrically conductive compound was produced according to the process described in B 40 (1907), 26 77.

#### Example 2

A commercial polyester film coated on one side with a hot-melt adhesive ("Heat-sealing Tape 318 H5," commercial product of the Nitto Company; total thickness:  $\sim 45 \mu\text{m}$ ; thickness of the hot-melt adhesive layer:  $\sim 25 \mu\text{m}$ ) was coated on both sides by knife coating with a solution of 0.15 g of emeraldine hydrochloride and 0.1 g of polyvinyl acetate in 12 ml of methanol (wet-film thickness: about  $25 \mu\text{m}$ , corresponding to a dry-film thickness of  $1-2 \mu\text{m}$ ). After evaporation of the solvent, a transparent film is obtained; surface resistance of the film on both sides:  $\sim 10^6 \Omega$ .

The film can be tightly sealed onto another plastic film--e.g., a polyester film--by heat sealing at  $120^\circ\text{C}$ .

#### Example 3

10 g of conductive soot (Vulcan XC 72, commercial product of the Kabot Company), 15 g of polyvinyl acetate (Movilith 50, commercial product of the Hoechst Company), 100 g of acetone, and 100 g of isopropanol were ground for 2 hours in a bead mill. The suspension was diluted in a ratio of 1:1 with a 1:1 mixture of isopropanol/acetone and applied on two sides by knife coating onto the polyamide film described in example 1 (wet-film thickness: about  $25 \mu\text{m}$ , corresponding to a dry-film thickness of  $1-2 \mu\text{m}$ ). After evaporation of the solvent, a film was obtained whose surface resistance  $R_{\text{op}}$  on both sides is  $1.4 \times 10^5 \Omega$ . The film can easily be bonded by heat sealing.

#### Example 4

10 g of electrically conductive tin oxide (commercial product of the Mitsubishi Metal Corporation), 5 g of polyvinyl acetate (Movilith 50, commercial product of the Hoechst Company) and 100 g of methylethyl ketone were ground for 5 hours in a bead mill. The obtained suspension was applied by knife coating to the polyamide film coated with hot-melt adhesive and described in example 1 (wet-film thickness: about  $25 \mu\text{m}$ , corresponding to a dry-film thickness of about  $1 \mu\text{m}$ ). After evaporation of the solvent, a film is obtained that has a surface resistance  $R_{\text{op}}$  of  $10^5 \Omega$  on both sides and that can easily be bonded by heat sealing.

Patent claims

1. Process for the production of molded plastic articles equipped with a hot-melt adhesive layer, characterized in that the hot-melt adhesive layer is provided with a 0.05-5  $\mu\text{m}$ -thick layer that makes up 10-100% by weight relative to the dry weight of the antistatic coating and contains electrically conductive compounds or solid materials, by coating with a solution of a soluble electrically conductive compound possibly containing a bonding agent or a dispersion of an electrically conductive, finely distributed solid material possibly containing a bonding agent, and subsequently removing the solvent or the dispersing agent.
2. Process according to claim 1, characterized in that the hot-melt adhesive layer is provided with a 0.05-2  $\mu\text{m}$ -thick layer that makes up 10-80% by weight relative to the dry weight of the antistatic coating and contains electrically conductive compounds or solid materials.
3. Process according to claim 1 or 2, characterized in that the thickness of the antistatic coating applied onto the hot-melt adhesive layer is maximally 50% of the thickness of the hot-melt adhesive layer.
4. Process according to claim 1 or 2, characterized in that the thickness of the layer applied to the hot-melt adhesive layer is 2-50% of the thickness of the hot-melt adhesive layer.
5. Process according to one of the claims 1-4, characterized in that polyanilinium salts or soluble electrically conductive polyheteroaromatics are used as soluble electrically conductive compounds and that conductive soots, electrically conductive metal oxides, or metal powders are used as electrically conductive, finely distributed solid materials.

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